ON-LINE HYDRIDE GAS PROCESS MONITOR FOR

SILICON AND COMPOUND SEMICONDUCTOR FABRICATION

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PHASE I

INTERIM TECHNICAL REPORT

May 1, 1995

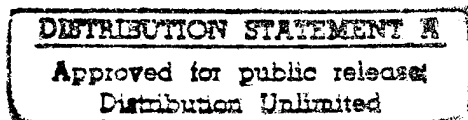Sponsored by

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Introduction

The fabrication of silicon and gallium arsenide compound semiconductors requires the use of hydride gas precursors such as arsine, phosphine, and silane. The accurate sensing of the concentration of these gases is essential for high yield device fabrication. Presently the methods for detecting these gases for on-line process control are very expensive ($18,000 to $35,000). These units are based on ultrasonic time of flight measurements, mass spectrometry, or FTIR spectrometry. Some of these sensor technologies are prone to coating of the sensor element so that their accuracy decreases with time. Other sensors do not operate below atmospheric pressure.

The inability to monitor and control the concentration of these gases directly affects the process repeatability and hence the quality of the semiconductors fabricated. This is especially true with ternary and quaternary compound optoelectronic materials such as AlGaAs and AlGaInAs, where the stoichiometry of each element must be correct for the device to be fabricated as desired. Therefore, development of an on-line sensor for process monitoring and control will enhance productivity of semiconductor manufacturing. The sensor will find applications in chemical vapor deposition (CVD), gas phase molecular beam epitaxy (MBE), silicon doping, and plasma deposition equipment.

In Phase I of this project, we compare five low-cost technologies for their ability to accurately measure semiconductor gas concentrations. The technologies are:

1. Fiber Optic-Based UV Adsorption
2. Solid Electrolyte Electrochemical Detector
3. Surface Photovoltage
4. Impedance Measurements
5. SAW/Flexial Beam Resonant Sensor

Description of Progress:

1. Fiber Optic-Based UV Adsorption

This approach is based on the adsorption of both phosphine and arsine in the ultraviolet. The extinction coefficient for both gases becomes significant at 220 nm, and rises sharply at lower wavelengths. The rate of the increase is different for the two gases. Therefore, absorption measurements could be used to calculate phosphine or arsine concentrations in a diluting gas. Since UV light sources, photodetectors and narrow bandwidth optical filters are readily available, this method meets the low cost criteria. Toward this end we purchased a Hamamatsu S1336 photodiode, and an Acton Research narrow bandwidth filter. A Fiberguide fiber optic bundle directs the UV light in and out of the hydride gas mixture through gas-tight union-cross fittings.

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Based on earlier absorption data we formulated a Beer's law type model for the hydride absorption. Fitting the earlier data to the model provided the extinction coefficient values (as a function of wavelength).

In these experiments we used an optical filter with a peak transmittance of 200 nm. A gas cylinder of 50% phosphine/50% hydrogen at was used to determine the absorption of the phosphine as a function of concentration. The total gas pressure, and hence, phosphine concentration was investigated from 0 to 30 psig. In the previous report, we showed a Beer's Law plot of absorbance vs. concentration for concentrations up to 0.06 mole/L.

In this report we extended the concentration range from 0 to 0.14 mole/L (equivalent to 30 psig pressure) for both arsine and phoshpine. These data are shown in Figures 1 and 2.

2. Palladium Hydride Sensor

Upon contact with palladium, hydrogen dissociates and absorbs into the palladium lattice thereby changing the resistivity of the palladium. We believe that hydrides such as phosphine and arsine will also dissociate when in contact with palladium:

$$PH_3 = P + 3H$$

$$AsH_3 = As + 3H$$

and

$$Pd + H = PdH$$
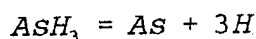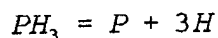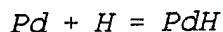
By analogy to the resistance change after absorbing hydrogen, we expect a decrease in resistance of a palladium wire by about 2% when it is saturated with either phosphine or arsine. The resistance of the 0.01 cm diameter palladium wire per centimeter is found through the conductivity of the wire:

$$p = \frac{1}{g} = 0.095x10^{-6} \ ohm^{-1}-cm^{-1}$$

and

$$resistance = p*\frac{L}{A} = .134 \ ohm/cm$$

A 2% change in the resistance of the wire would therefore result in a .003 ohm change per centimeter. To reverse the effect of hydrogen saturation of the palladium wire by driving a small current through it.

A 2.3 cm X 0.01 cm diameter palladium wire was mounted on a plastic rod placed inside a swagelock stainless steel union cross fitting. The test gas was pumped through the other leg of the union cross. The A.C. resistance of the wire was measured with an Hewlett Packard 4274A LCR meter at 100 KHz.

The system was flushed with nitrogen for 10 minutes at a rate of 1 liter per minute. Next, the tubing was filled with 30 psig phosphine or arsine. This was repeated three times. Changes in resistance of the wire were recorded. We observed no changes in resistance with either hydrogen or the hydrides.

Because of the lack of response of the palladium wire, we decided to increase the length of the palladium wire to 21 cm. This, we predicted, would result in a hydride-induced change of .06 ohms, a signal which would be much more easily detected.

Our procedure changed slightly for this run. We first de-gassed the wire by pre-heating it with a 500 mA current for 10 minutes while flushing with nitrogen. After three repetitions of heating the wire while flushing, and exposing it to phosphine, we saw no change within the expected magnitude of the resistance of the wire. We also tested the effects of hydrogen on the wire, following the procedure given above, and found no change in resistance of the wire within the expected magnitude.

3. Oxide Bronzes in Hydride Sensors

Like palladium, some oxides have the ability to dissociate hydrogen to form a solid compound. Molybdenum oxide, vanadium oxide, and tungsten oxide form bronze-like crystal structures when exposed to hydrogen. The reaction is:

$$\frac{1}{2}H_2(g) + \frac{1}{0.30}MoO_3(s) = \frac{1}{0.3}H_{0.3}MoO_3(s)$$
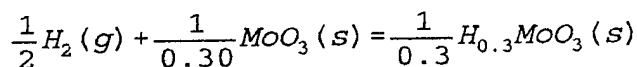
We speculated that these oxides would react with hydrides (arsine, phosphine) to form similar oxide bronzes. Monitoring the resistance change of the bronzes when exposed to the hydrides could provide a reversible detector. As a first step we exposed oxide powders to hydrogen and the hydrides.

A 0.3 liter test vessel served as a chamber to expose the oxide bronzes to the gases. A scrubber was connected through a valve to one of the two gas outlets on the otherwise vacuum tight vessel. The other outlet was connected, also through a valve, to a regulator

which could accommodate both arsine and phosphine cylinders. The scrubber was vacuum tight, and the vessel could be evacuated through the scrubber.

0.01 moles of each oxide were weighed and placed in small ceramic crucibles. After evacuation the desired gas was slowly added. When the vessel reached 0 psig, the valves on the gas outlets of the vessel were closed. After 10 hours the vessel was flushed with nitrogen to clear it of the test gas. The samples were removed and weighed.

An interesting side observation is that the oxides change color when exposed to the various gases. These changes are listed in the table below. Only the molybdenum oxide shows sufficient change to possibly use its color as a reversible hydride detector.

Our next experiments will focus on pressing a solid from the molybdenum oxide powder. We will then measure its A.C. resistance and the reversibility of the resistance when exposed to different concentrations of the hydrides. We will also attempt to measure the direct current associated with protons migrating through the bronze.

Color Change for Oxides

	Original	Hydrogen	Phosphine	Arsine
MoO_3	light green	med. blue	light blue	dark blue
WO_3	light green	N. C.	N. C.	slightly darker
V_2O_5	orange	brown-orange	N. C.	black

N. C. = no change

4. Capacitance Hydride Gas Monitor

The dipole moment of phosphine and arsine are 0.55 and 0.15 Debye respectively. The dielectric constant is related to the gas dipole moment through the Debye equation for total molar polarizability. The capacitance of chamber consisting of two plates of area, A, separated by a distance, d, with a material of a dielectric constant, ϵ, between them is:

$$C = \epsilon \times \frac{A}{d}$$

We speculated that we could detect changes in arsine or phosphine concentration by measuring the capacitance of a test cell. For the test cell we used a vane type air-dielectric capacitor with A = 100 cm^2 and d = 0.1 cm. This was mounted in an air tight stainless steel vessel of 0.36 liters with two gas inlets and two gas tight insulated electric feedthroughs on the removable top. The capacitor was epoxied to the removable top, and the insulated feedthroughs were soldered to the capacitor leads. The capacitance was measured with a HP-

4274A high-precision LCR meter. Gas pressures of 0 to 30 psig in 5 psig intervals corresponding to concentrations of 0 to 30 mole/L were tested.

We first tested N_2 and H_2 for a correlation between measured capacitance and dielectric constant. Then we repeated the N_2 and H_2 runs and followed them with PH_3 and AsH_3. These results are also shown in Figure 3.

The dielectric constants for nitrogen and hydrogen are:

$$\epsilon_{N_2}=1.00058$$

$$\epsilon_{H_2}=1.00026$$

Our N_2 curve yielded a capacitance variation with concentration of .0623 pF per mol/L. Our H_2 curve yielded a slope of 7 pF per mol/L. The ratio of the slopes is:

$$\frac{slope_{N_2}}{slope_{H_2}}=2.17$$

The ratio of the theoretical dielectric constants is:

$$\frac{\epsilon_{N_2}-1}{\epsilon_{H_2}-1}=2.2$$

Hence, the measured capacitance correlates well with the dielectric.

We were not able to find published data for the dielectric constant for arsine and phoshpine. However, the good correlation for the hydrogen and nitrogen data gives us confidence that the measured capacitance for arsine and phosphine accurately correlate with their dielectric constants.

As shown by the figures measurement of the gas, capacitance is linear in concentration and reversible. Hence this method looks very promising for a hydride detector.

Summary

At this stage, the UV absorption and gas dielectric/capacitance seem to be the most promising methods. Both measurements are reversible and have linear response with hydride concentration.

Our next experiments will complete the oxide bronze measurements, and carry out the SAW/resonant detector measurements. After these experiments we will rank the various methods in preparation for more detailed investigation and building the prototype detectors in Phase II.

Change in Key Personnel:

None.

Summary of Substantive Information Derived from Special Events:

No conferences were attended, nor papers delivered during this report period.

Problems Encountered and/or Anticipated:

None.

Action Required by the Government:

None.

Fiscal Status:

Amount of contract	$	70,576.00
Invoiced to government		47,051.00
Balance	$	23,525.00

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AsH3 Beer's Law Data
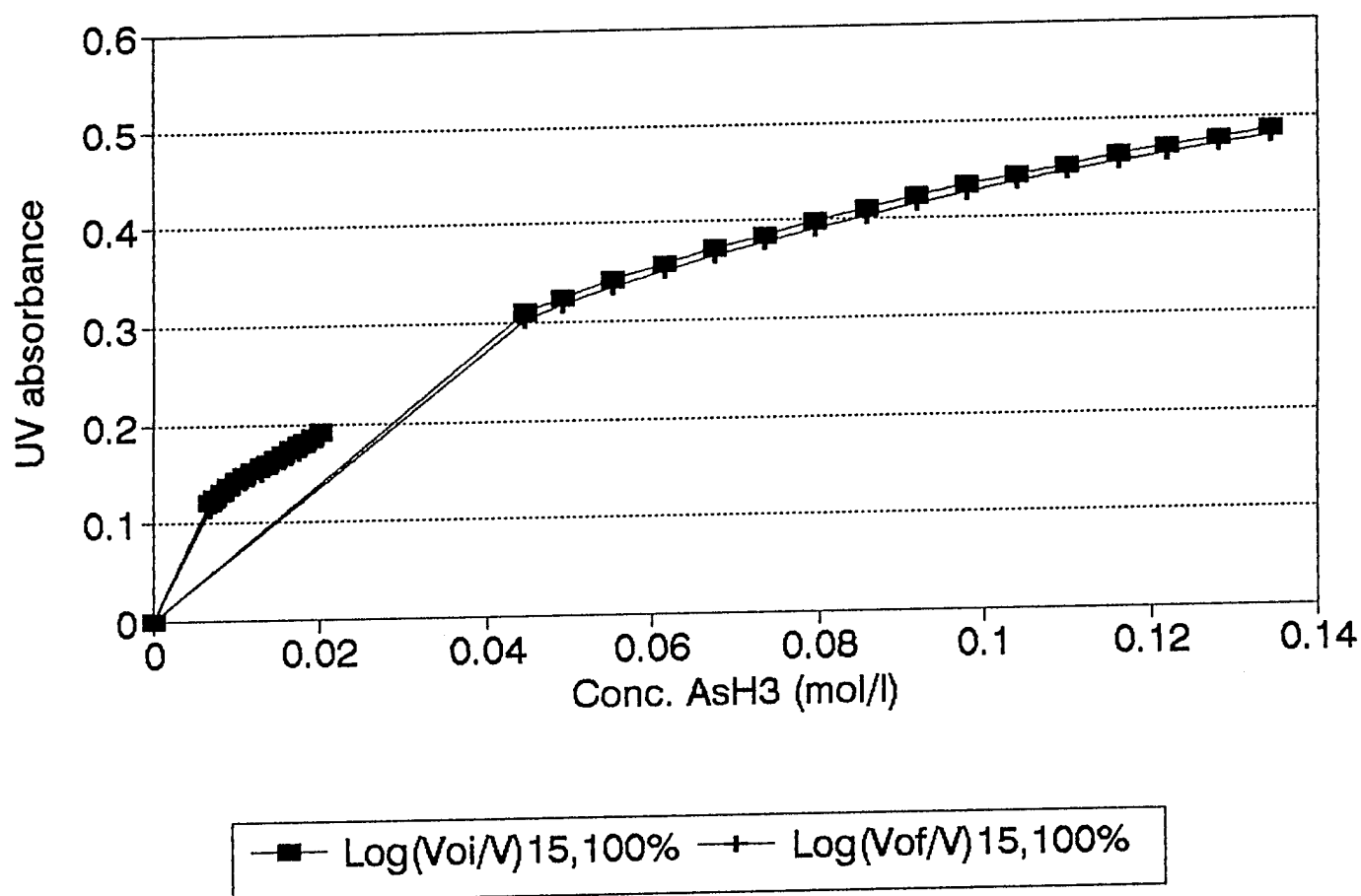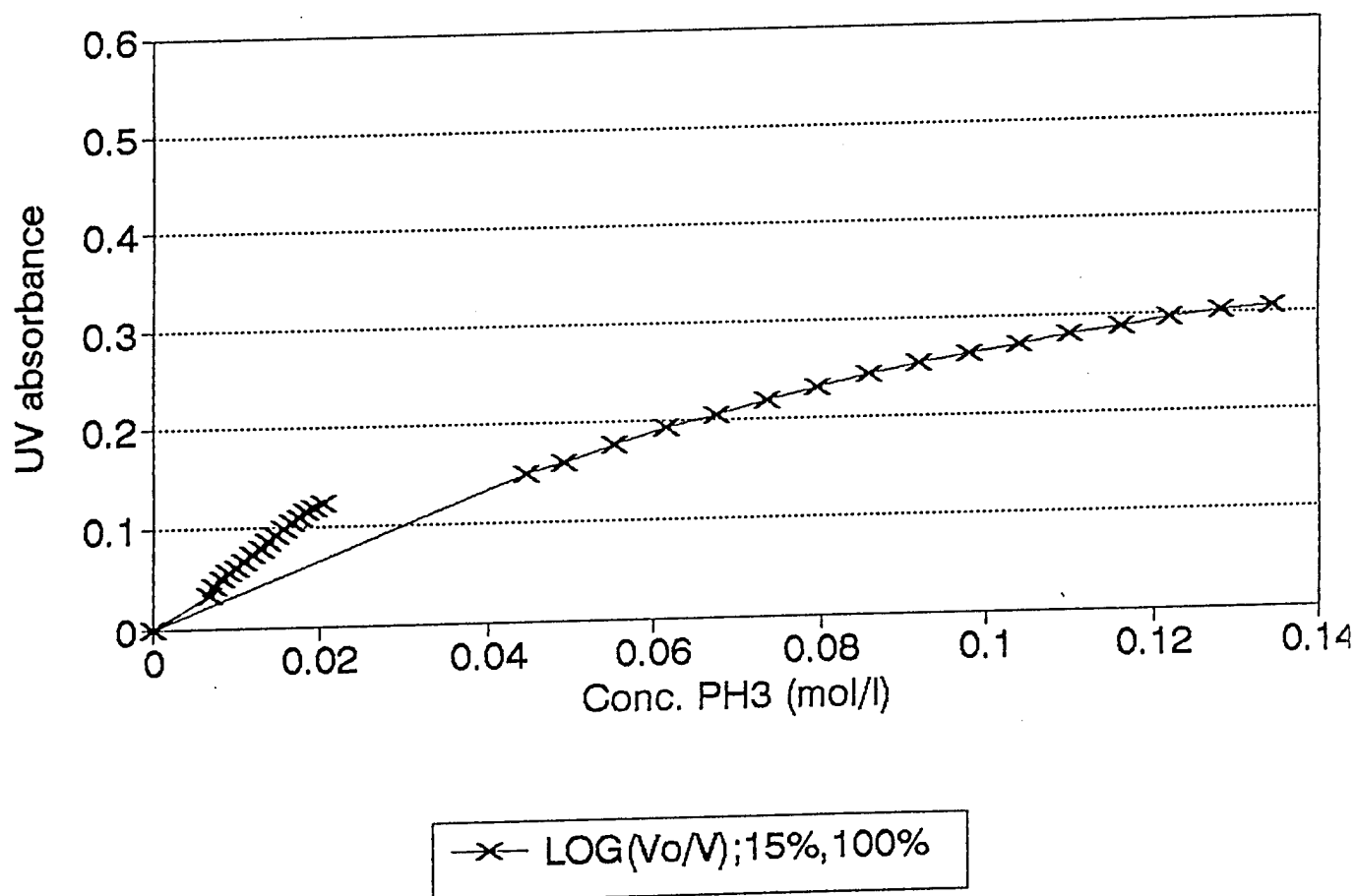## in flowing AsH3

FIGURE 1

PH3 Beer's Law Data
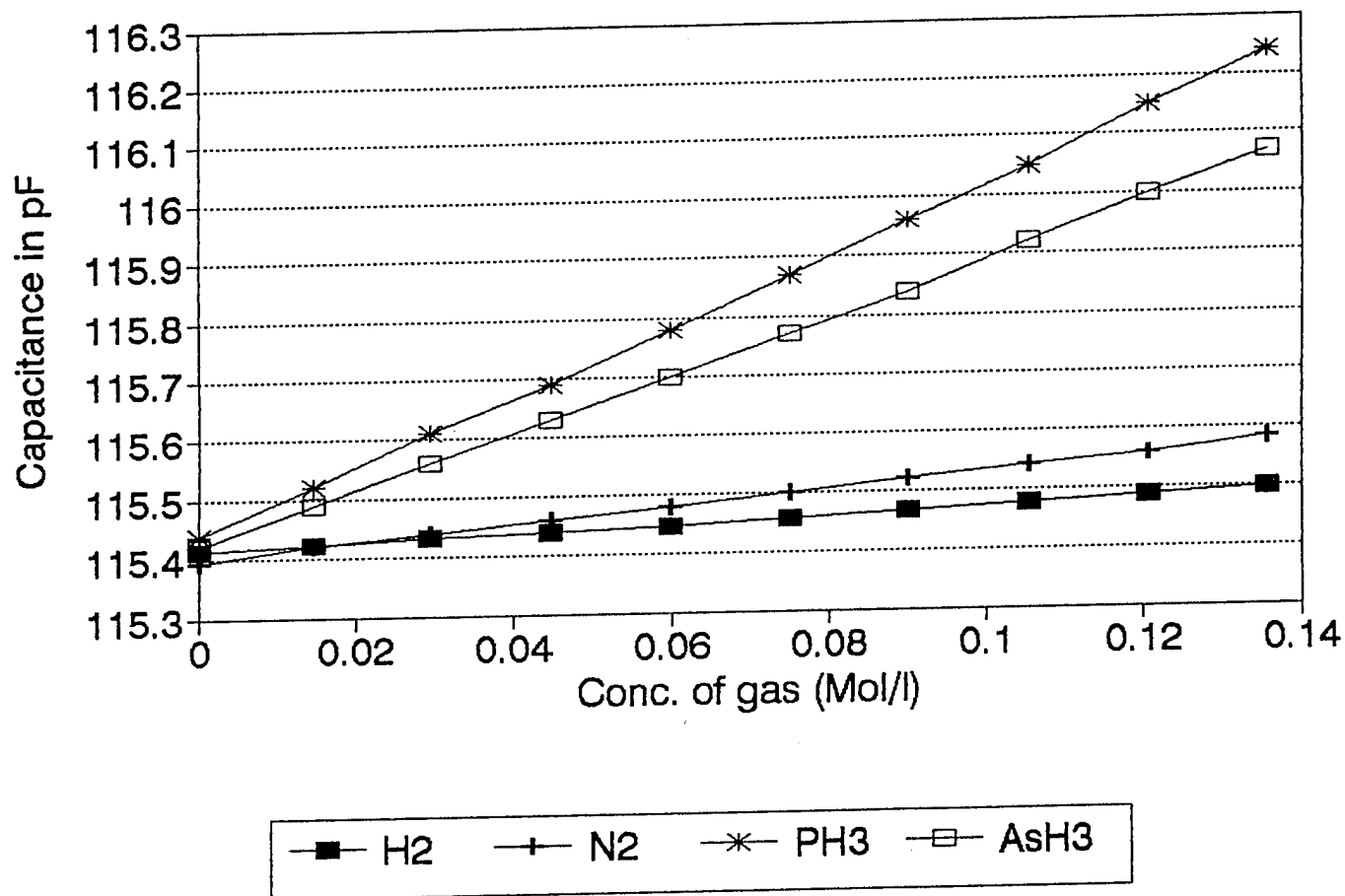## in flowing PH3

FIGURE 2

Dielectric Data

FIGURE 3